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(19) (CA) **APPLICATION FOR CANADIAN PATENT** (12)

(54) **Radiation-Curable Aqueous Polyurethane Emulsions**

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Radiation-curable aqueous polyurethane emulsions

Abstract

A water-dispersable, radiation-curable polyurethane, essentially comprises

- a) organic polyisocyanates,
- b) polyesterpolyols,
- c) if required, polyols differing from b)
- d) compounds having at least one group reactive toward isocyanate and at least one carboxyl or carboxylate group,
- e) compounds having at least one group reactive toward isocyanate and at least one copolymerizable unsaturated group and
- f) if required, compounds differing from a) to e) and having at least one group reactive toward isocyanate,

the K value of the polyurethane being less than 40 and the content of copolymerizable unsaturated groups being from 0.01 to 0.4 mol/100 g of polyurethane (solid) and at least the components a), b) and e) being reacted in one stage in the preparation of the polyurethane.

Radiation-curable aqueous polyurethane emulsions

The present invention relates to a water-dispersable, radiation-curable polyurethane, essentially comprising

- a) organic polyisocyanates,
- b) polyesterpolyols,
- 10 c) if required, polyols differing from b)
- d) compounds having at least one group reactive toward isocyanate and at least one carboxyl or carboxylate group,
- e) compounds having at least one group reactive toward isocyanate and at least one copolymerizable unsaturated group and
- 20 f) if required, compounds differing from a) to e) and having at least one group reactive toward isocyanate,

the K value of the polyurethane being less than 40 and the content of copolymerizable unsaturated groups being from 0.01 to 0.4 mol/100 g of polyurethane (solid) and at least the components a), b) and e) being reacted in one stage in the preparation of the polyurethane.

- 30 The present invention also relates to a process for the preparation of polyurethanes and to the use of the polyurethanes as coating materials.

EP-A 26 313 and EP-A 554 784 disclose aqueous polyurethane emulsions and their use as coating materials. According to their content of sulfonic acid or sulfonate groups, the polyurethanes described are highly hydrophilic, resulting in insufficient wet strength of coatings.

- 40 Polyurethanes which have carboxyl groups as the dispersing-active component have also been unsatisfactory to date in their performance characteristics. For example, polyurethane emulsions according to EP-A 392 352, EP-A 181 486 and EP-A 209 684 have disadvantages with regard to the resistance to chemicals and the mechanical properties, for example the hardness, the elasticity and the flexibility of coatings.

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It is also desirable for the emulsions to give a dry and nontacky film after drying and after evaporation of the water in air before the film is cured using high-energy radiation. This is important for thin coatings on substrates which have a finely structured surface, for example wood and leather. In these cases, it is very often desired to obtain an open-pore coating which reveals the fine structure of the surface even after the coating procedure.

- 10 Particularly on surfaces having relatively large profile depths (groove-and-tongue boards), there are areas into which the high-energy radiation cannot penetrate, so that there too normal drying should be able to produce a nontacky and dry film.

It is an object of the present invention to provide polyurethane emulsions which give coatings having good wet strength, resistance to chemicals and good mechanical properties. Furthermore, the coatings should be nontacky and dry after physical drying of the applied polyurethane emulsions, ie. without radiation curing.

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We have found that this object is achieved by the polyurethane emulsions defined at the outset, a process for their preparation and their use for the production of coatings.

The polyurethane essentially comprises components a) to f).

- Examples of suitable polyisocyanates a) are straight-chain or branched C₄-C₁₄-alkylene diisocyanates, cycloaliphatic diisocyanates having a total of 6 to 12 carbon atoms, aromatic diisocyanates having a total of 8 to 14 carbon atoms, isocyanurate-containing polyisocyanates, uretdione diisocyanates, biuret-containing polyisocyanates, polyisocyanates containing urethane and/or allophanate groups, polyisocyanates containing oxadiazine-trione groups, uretonimine-modified polyisocyanates or mixtures thereof.
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- Examples of diisocyanates are tetramethylene diisocyanate, hexamethylene diisocyanate (1,6-diisocyanatohexane), octamethylene diisocyanate, decamethylene diisocyanate, dodecamethylene diisocyanate, tetradecamethylene diisocyanate, trimethylhexane diisocyanate or tetramethylhexane diisocyanate, cycloaliphatic diisocyanates, such as 1,4-, 1,3- or 1,2-diisocyanatocyclohexane, 4,4'-di(isocyanatocyclohexyl)methane, 1-isocyanato-3,3,5-trimethyl-5-(isocyanatomethyl)cyclohexane (isophorone diisocyanate) or 2,4- or 2,6-diisocyanato-1-methylcyclohexane, or aromatic diisocyanates, such as 2,4-diisocyanatotoluene, 2,6-diisocyanatotoluene, tetramethylxylylene diisocyanate, 1,4-diisocyanatoben-
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zene, 4,4'- and 2,4-diisocyanatodiphenylmethane, p-xylylene diisocyanate and isopropenyldimethyltolylene diisocyanate.

The isocyanurate-containing polyisocyanates are in particular simple trisisocyanatoisocyanurates, which are cyclic trimers of the diisocyanates, or mixtures with their higher homologs having more than one isocyanurate ring. The isocyanatoisocyanurates generally have an NCO content of from 10 to 30, in particular from 15 to 25, % by weight, and an average NCO functionality of, 10 from 3 to 4.5.

Uretidione diisocyanates are cyclic dimerization products of diisocyanates. The uretidione diisocyanates can be used, for example, as the sole component or as a mixture with other polyisocyanates, in particular the isocyanurate-containing polyisocyanates.

Suitable biuret-containing polyisocyanates preferably have an NCO content of from 18 to 22% by weight and an average NCO functionality of from 3 to 4.5. 20

Polyisocyanates containing urethane and/or allophanate groups can be obtained, for example, by reacting excess amounts of diisocyanates with simple polyhydric alcohols, for example trimethylolpropane, glycerol, 1,2-dihydroxypropane or mixtures thereof. These polyisocyanates having urethane and/or allophanate groups generally have an NCO content of from 12 to 20% by weight and an average NCO functionality of from 2.5 to 3.

30 Polyisocyanates containing oxadiazinetriene groups can be prepared from diisocyanate and carbon dioxide.

The stated polyisocyanates may also preferably be used in the form of a mixture.

Preferred polyisocyanates are diisocyanates and (cyclo)aliphatic polyisocyanates having a higher functionality.

Polyisocyanates containing isocyanurate, urethane and biuret 40 groups, for example hexamethylene triisocyanurate, biurets based on hexamethylene diisocyanate and urethane-containing polyisocyanates based on hexamethylene diisocyanate are particularly preferred.

Mixtures of diisocyanates, for example hexamethylene diisocyanate and isophorone diisocyanate, with polyisocyanates having a higher functionality in a weight ratio of from 95:5 to 5:95, in

particular 50:50, are also particularly preferred.

- The polyesterpolyols b) are in particular polyesterdiols, preferably reaction products of dihydric alcohols with dibasic carboxylic acids. Instead of the free polycarboxylic acids, the corresponding polycarboxylic anhydrides or corresponding polycarboxylates of lower alcohols or mixtures thereof may also be used for the preparation of the polyester polyols. The polycarboxylic acids may be aliphatic, cycloaliphatic, aromatic or
- 10 heterocyclic and may be unsubstituted or substituted, for example by halogen, and/or unsaturated. Examples of these are succinic acid, adipic acid, suberic acid, azelaic acid, sebacic acid, phthalic acid, isophthalic acid, phthalic anhydride, tetrahydrophthalic anhydride, hexahydrophthalic anhydride, tetrachlorophthalic anhydride, endomethylenetetrahydrophthalic anhydride, glutaric anhydride, maleic acid, maleic anhydride, fumaric acid and dimeric fatty acids. Examples of suitable polyhydric alcohols are ethylene glycol, 1,2- and 1,3-propylene glycol, 1,4- and 1,3-butanediol, 1,4-butanediol, 1,4-butyne-2,3-diol, 1,5-pentanediol,
- 20 1,6-hexanediol, 1,8-octanediol, neopentylglycol, cyclohexanedi-methanol (1,4-bis(hydroxymethyl)cyclohexane), 2-methyl-1,3-propanediol, 1,5-pentanediol and diethylene glycol, triethylene glycol, tetraethylene glycol, polyethylene glycol, dipropylene glycol, polypropylene glycol, dibutylene glycol and polybutylene glycols.

- The number average molecular weight M_n of the polyesterpolyols is preferably from 500 to 5000, particularly preferably from 750 to 3000, g/mol. The nonuniformity M_w/M_n is preferably greater than 1 and particularly preferably greater than 1.5. The value of 8 is
- 30 in general not exceeded. M_n and M_w are determined by gel permeation chromatography (polystyrene standard, eluent tetrahydrofuran, UV detection).

Furthermore, polyols c) are, for example, low molecular weight diols or triols, in particular having a molecular weight of less than 500 g/mol, which are used as chain extenders or crosslinking agents. For example, the diols stated above as components of the polyester are suitable.

- 40 Compounds which contain at least one group reactive toward isocyanate groups, preferably one or two such reactive groups, ie. hydroxyl or primary or secondary amino groups, and at least one, preferably one, carboxyl or carboxylate group are used as further component d).

Examples are hydroxycarboxylic acids, such as dihydroxycarboxylic acids, eg. dimethylolpropionic acid, or aminocarboxylic acids. Aminocarboxylic acids are preferred, diaminocarboxylic acids being particularly preferred. Adducts of acrylic acid with C₂-C₆-alkylenediamines or preferably C₂-alkylenediamines, in a molar ratio of alkylenediamine to acrylic acid of, preferably about 1:1 (PUD salt) are very particularly preferred.

Component d) renders the polyurethanes self-dispersible, ie. in this case no dispersant, such as protective colloids or emulsifiers, are required for dispersing in water.

Carboxyl groups are neutralized before or during the dispersing in water, for example by inorganic and/or organic bases, such as alkali metal hydroxides, alkali metal carbonates, alkali metal bicarbonates, ammonia or primary, secondary or, preferably, tertiary amines, such as triethylamine.

Examples of suitable components e) which have at least one, preferably one, copolymerizable unsaturated group and at least one, preferably one, group reactive toward isocyanate are esters of acrylic or methacrylic acid with polyols, at least one hydroxyl group remaining unesterified. Hydroxy-C₁-C₁₂-alkyl (meth)acrylates are particularly preferred, and the alkyl chains are linear or branched.

The components f) which are to be used if required are, for example, at least difunctional amine chain extenders or cross-linking agents, preferably having a molecular weight of from 32 to 500 g/mol, which contain at least two primary, or two secondary amino groups or one primary and one secondary amino group.

Examples of these are diamines, such as diaminoethane, diaminopropanes, diaminobutanes, diaminohexanes, piperazine, 2,5-dimethylpiperazine, amino-3-aminomethyl-3,5,5-trimethylcyclohexane (isophoronediamine, IPDA), 4,4'-diaminodicyclohexylmethane, 1,4-diaminocyclohexane, aminoethylethanolamine, hydrazine, hydrazine hydrate or triamines, such as diethylenetriamine or 1,8-diamino-4-aminomethyloctane.

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The amounts of the individual components may be suitably expressed in gram equivalents of those groups of components b) to f) which are reactive toward isocyanate, based on 1 gram equivalent of polyisocyanate a), and are:

- b) preferably from 0.1 to 0.8, particularly preferably from 0.2 to 0.7, gram equivalent of hydroxyl groups,
 - c) preferably from 0 to 0.8, particularly preferably from 0 to 0.7, gram equivalent of hydroxyl groups and
 - f) preferably from 0 to 0.4, particularly preferably from 0 to 0.2, gram equivalent of groups reactive with isocyanate.
- 10 Components d) are preferably used in amounts such that the polyurethane contains from 0.005 to 0.1, particularly preferably from 0.01 to 0.03, mol of carboxyl or carboxylate groups per 100 g of polyurethane.
- Compounds e) are preferably used in amounts such that the content of double bonds in the polyurethane is preferably from 0.1 to 0.3, particularly preferably from 0.15 to 0.25 mol per 100 g of polyurethane.
- 20 The molar ratio of isocyanate groups to the groups reactive with isocyanate in all components b) to f) (essentially hydroxyl groups and primary and secondary amino groups) is preferably from 1:0.8 to 1:1.2, particularly preferably about 1:1.

- The novel polyurethane is prepared by reacting at least components a), b) and e) in one stage. For example, components b) and e) may be initially taken, the polyisocyanate being metered in during the reaction. It is important that components b) and e) and, if required also c) are in competition during the reaction
- 30 and are reacted simultaneously with the polyisocyanate. This is an important condition for establishing a broad molecular weight distribution of the polyurethane.

Component d) is preferably added only toward the end of the reaction.

The course of the reaction can be monitored through the decrease in the content of functional groups, in particular of isocyanate groups.

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The reaction is preferably carried out in an inert, water-miscible solvent, such as acetone, tetrahydrofuran, methyl ethyl ketone or N-methylpyrrolidone. The reaction temperature is in general from 20 to 160°C, preferably from 50 to 100°C.

The usual catalysts, such as dibutyltin dilaurate, tin(II) octoate or diazabicyclo[2.2.2]octane, may be used for accelerating the reaction of the diisocyanates.

The novel polyurethane has a K value of less than 40, preferably less than 35. The K value is preferably greater than 2, in particular greater than 5. The particularly preferred range is from 20 to 30. The K value is determined in 1% strength by weight solution in dimethylformamide according to Fikentscher,

10 Cellulosechemie 13 (1932), 58.

The novel polyurethane has a broad molecular weight distribution. The quotient of the weight average molecular weight M_w and the number average molecular weight M_n is a measure of the distribution. M_w/M_n is preferably greater than 1.5, particularly preferably greater than 2. In general, however, the distributions of less than 6 are sufficiently broad.

M_n and M_w are determined by gel permeation chromatography (polystyrene standard, eluent: tetrahydrofuran, UV detection).

Carboxyl groups are converted into the corresponding ions by, for example, neutralization with bases or acids before or during the dispersing of the polyurethane in water.

After the dispersing, the organic solvent can, if desired, be distilled off. Substantially solvent-free aqueous emulsions are preferred.

30 The polyurethane content of the emulsions may be in particular from 5 to 70, preferably from 20 to 50, % by weight, based on the emulsion.

The novel emulsions may contain further additives, for example pigments, dyes, fillers, and assistants conventionally used in coating technology.

Photoinitiators are added to the emulsions for radiation curing by UV light.

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Examples of suitable photoinitiators are benzophenone, alkylbenzophenones, halomethylated benzophenones, Michler's ketone, anthrone and halogenated benzophenones. Benzoin and its derivatives are also suitable. Other effective photoinitiators are anthraquinone and many of its derivatives, for example β -methylanthraquinone, tert-butylanthraquinone and anthraquinonecarboxy-

lates, and acylphosphine oxides, eg. 2,4,6-trimethylbenzoyl-diphenylphosphine oxide (Lucirin® TPO).

The photoinitiators which, depending on the intended use of the novel materials, are generally used in amounts of from 0.05 to 20, preferably from 0.05 to 5, % by weight, based on the polyurethane, may be used as individual substances or, owing to frequent advantageous synergistic effects, also in combination with one another.

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Advantageous additives which may lead to a further increase in the reactivity are tertiary amines, eg. triethylamine and triethanolamine. They too are generally used in amounts of up to 5% by weight, based on the polyurethane.

It should furthermore be mentioned that the novel emulsions can also be thermally crosslinked if they contain initiators which form free radicals at elevated temperatures. For example, dibenzoyl peroxide, cumyl hydroperoxide or azobisisobutyronitrile may be used. Other examples of suitable initiators are described in Polymer Handbook, 2nd edition, Wiley & Sons, New York.

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The novel emulsions can be used for the production of moldings and, preferably, coatings.

They can be applied to substrates such as metal, plastic, glass, wood, paper, board, leather or textile, for example by spraying, pouring, printing or knife-coating.

30 In the case of radiation curing, the coatings are generally preheated for up to 30 minutes at up to 100°C, during which time they dry physically, ie. without chemical crosslinking, and are then exposed briefly to UV or high-energy electron radiation. For this purpose, the UV or electron radiation sources usually used for curing of coatings are employed.

In the case of porous substrates, for example leather, paper or wood, only very short times are generally required for the physical drying since the main amount of the water is absorbed by

40 the substrate.

Physical drying is sufficient to convert the novel polyurethanes into a substantially nontacky, dry coating.

After the radiation curing, the coating has very good wet strength, good resistance to chemicals and good mechanical properties, for example good hardness, tensile strength,

resilience, flexibility and good adhesion. Surprisingly, good flexibility and adhesion are achieved in combination with high hardness.

After the radiation curing, the coatings exhibit only slight shrinkage. On bottomed leather, good wet rub fastness (at more than 500 rubbing cycles with moist felt) and resistance to flexing (no damage and no detachment of the coating on frequent flexing of the leather) were found.

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Examples

Preparation of the polyurethane emulsion

Polyurethane emulsion 1

- 6.74 g of a polyester obtained from isophthalic acid, 1,6-hexanediol and adipic acid and having a number average molecular weight of about 2000 and a weight average molecular weight of about 10,000 (GPC), 3.26 kg of 1,4-butanediol, 7.83 kg of 2-hydroxyethyl acrylate, 16.6 kg of acetone, 31.2 g of hydroquinone monomethyl ether, 19.4 g of dibutyltin dilaurate and 58.2 g of 2,6-di-*t*-butyl-*p*-cresol were initially taken in a stirred kettle. The content was preheated to 60°C and the mixture of 15.91 kg of isophorone diisocyanate with 4.98 kg of Basonat PLR 8638 (trimerized HDI) was added dropwise in the course of 2 hours. After the isocyanate content of the mixture had decreased to 1.15% after a further 1.5 hours after the end of the addition, 3.16 kg of PUD salt in the form of 40% strength aqueous solution were added in the course of 10 minutes. After a further 20 minutes, 47.7 kg of distilled water were added in the course of 10 minutes, the interior was heated to 65°C and an acetone/water mixture was distilled off, reduced pressure of about 100 mbar finally being applied to avoid frothing. The loss of the water distilled off was then compensated by further addition. The content was still highly viscous (from 1.5 to 2.5 Pa.s) owing to the incorporated urea bonds and their hydrogen bridge bonds but lost this viscosity as a result of stirring for 1.5 hours at 75°C and reached a final value of about 50 mPa.s. The emulsion obtained was pale, opaque and bluish and had particle sizes from 70 to 150 nm. The molecular weight of the polyurethanes was about 2000 (number average) and about 5000 (weight average) (polydispersity about 2.5).

Polyurethane emulsions 2 to 4

The preparation corresponded to that of polyurethane emulsion 1. As stated in Table 1, the content of hydroxyethyl acrylate was reduced and the latter amount was replaced with an amount of butanediol which was equimolar relative to the OH groups. Where necessary, the emulsions were brought to a polyurethane content of 40% by weight with water. 0.4 g of a photoinitiator (Irgacure® 500) was added to 25 g of the emulsions. The emulsions were

10 applied to polyester film using a 200 µm box doctor and were dried at 60°C for 20 minutes in a through-circulation oven. The coatings, on a conveyor belt (10 m/min), were then exposed to 2 UV lamps (80 W/cm). The dry film thickness was about 50 µm. The self-supporting clear coating films were detached from the film and cut into strips 12.5 cm wide and 15 cm long. 10 test strips in each case were tested in a universal tester 81802 from Frank, and the tensile test (elongation at break, tensile strength) according to DIN 53 455 and the determination of the modulus of elasticity according to DIN 53 457 were carried out.

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The pendulum hardness was determined according to DIN 53 157. It is a measure of the hardness of the coating (high values: great hardness).

The Erichsen cupping was determined according to DIN ISO 1520. It is a measure of the flexibility and adhesion of the coating (high values: good flexibility).

The results are shown in Table 1.

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Table 1

Emulsion		1	2	3	4
Hydroxyethyl acrylate		7.83 kg	6.85 kg	5.87 kg	4.89 kg
Double bond content mol/100 g of polyurethane		0.169	0.150	0.130	0.110
10	Appearance of the emulsion	milky opaque	milky opaque	milky white	white, thixotropic
Solids content (% by weight)		40	40	35	32
Particle size (nm)		65.4	113.4	158.7	277.1
pH		8.19	7.61	7.97	8.03
K value (1% DMF)		22.2	25.2	30.4	29.5
Properties of the coating					
20	Tensile strength (N/mm ²)	59.9	60.5	55.7	54.1
Elongation at break (%)		3.47	3.35	3.53	3.55
Modulus of elasticity (N/mm ²)		2121	2082	1950	1715
Pendulum hardness (sec)		145	146	125	117
Erichsen value		7.6/7.9	7.0/7.0	0.6/0.6	0.6/2.1
30	Pencil hardness	2H	2H	H	H

We claim:

1. A water-dispersable, radiation-curable polyurethane, essentially comprising
 - a) organic polyisocyanates,
 - b) polyesterpolyols,
 - c) if required, polyols differing from b)
 - d) compounds having at least one group reactive toward isocyanate and at least one carboxyl or carboxylate group,
 - e) compounds having at least one group reactive toward isocyanate and at least one copolymerizable unsaturated group and
 - f) if required, compounds differing from a) to e) and having at least one group reactive toward isocyanate,the K value of the polyurethane being less than 40 and the content of copolymerizable unsaturated groups being from 0.01 to 0.4 mol/100 g of polyurethane (solid) and at least the components a), b) and e) being reacted in one stage in the preparation of the polyurethane.
2. A polyurethane as claimed in claim 1, wherein d) is an amino-carboxylic acid or a salt thereof.
3. A polyurethane as claimed in claim 1, wherein the amino-carboxylic acid is an adduct of acrylic acid with a C₂-C₆-alkylenediamine in a molar ratio of about 1:1.
4. A polyurethane as claimed in any of claims 1 to 3, wherein the content of carboxyl groups or salts thereof is from 0.005 to 0.1 mol/100 g of polyurethane (solid).
5. Aqueous emulsion of a polyurethane as claimed in any of claims 1 to 4.
6. A process for the preparation of a polyurethane as claimed in any of claims 1 to 4, wherein at least the components a), b) and e) are reacted in one stage.

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7. Use of a polyurethane as claimed in any of claims 1 to 4 or of an aqueous emulsion thereof as claimed in claim 5 as the coating material.